Liquid composition with fungicidal, bactericidal or bacteriostatic activity

Clms 9-1

The subject of the present invention is a liquid composition with fungicidal, bacteriostatic or bactericidal activity, and methods for the preparation and use of the composition.

It has long been known to use phytopharmaceutical products based on inorganic salts, oxides or hydroxides of copper, in particular for their fungicidal properties (vine downy mildew and the like) but also for their bactericidal power (bacterial canker of peach and apricot trees, bacteriosis of apple and pear trees caused by pseudomonas, and the like) or their bacteriostatic power which prevents bacterial diseases from becoming established.

The fungicidal and bactericidal activity of copper depends on the nature of the copper compound and on the quality of its manufacture.

The "Bordeaux mixture" has been used for over a century for the treatment of grape vine. First prepared by the viticulturist, and then manufactured industrially, it is obtained by accurately neutralizing a solution of copper sulfate with a milk of lime. This mixture, brought to neutrality (pH = 7) is then dried, ground and micronized.

Among the other products based on copper, there may be mentioned copper oxichloride, copper hydroxide, copper carbonate, copper(I) oxide, and the like.

These inorganic salts, oxides or hydroxides of copper, used alone or in combination with other compounds, are generally provided in the form of wettable powders, dispersible granules, suspension concentrates, dustable powders, and the like.

The inorganic salts, oxides or hydroxides of copper may also be combined with inorganic fungicides, in particular sulfur, or organic fungicides to form, in the latter case, organocopper compounds.

Among the organic active substances, there may be mentioned in particular folpel, maneb, mancozeb, propineb, zineb, cymoxanil, metiram-zinc.

The formulations are provided in the forms described above.

With the exception of the dustable powders, the other compositions generally comprise surfactants, wetting agents, dispersing agents, emulsifiers, antifoams and the like, which contribute to the stability of the formulations and then to the use of the products, and in particular to their dispersion in water for the production of mixtures for treatment.

In addition to the choice of inorganic salts, oxides or hydroxides of copper and to the selection of surfactants, formulators seek to enhance the efficacy of the products because the degree of protection from a copper compound against attacks by fungi and bacteria is closely related to its capacity to saturate the surface of the plant by forming a microscopic film of particles. Adherence to the plant followed by resistance to strong rain is also one of the objectives sought by the manufacturers.

For some time now, and in particular for the treatment of grape vine, many products using copper hydroxide as active substance have been appearing on the market.

The optimization of the formulations based on copper hydroxide, in particular of the suspension concentrates, has been carried out by:

- the search for a specific structure for the particles: crystallized fine needles, acicular structure;
- the improvement in the reduction of their size obtained by micronization or by a chemical method for manufacture of copper hydroxide, it being possible for said size to reach from 0.3 to 0.4 μm;
- the choice of the surfactants and co-formulants capable of stabilizing the formulation and of increasing the efficacy thereof.

FR 2 599 592 describes liquid formulations for the preventive and curative treatment of cryptogamic diseases of the oidium type comprising a lipophilic inorganic active substance consisting of fine ground or micronized sulfur, in suspension in a liquid composed of a mixture of pine oil and water, the pine oil enhancing the efficacy of the sulfur.

The work by the inventors which has led to the present invention has made it possible to establish that the efficacy of inorganic salts, oxides or hydroxides of copper can, surprisingly, be enhanced when these were combined with a terpenic derivative.

This discovery is unexpected insofar as persons skilled in the art did not expect the efficacy of inorganic salts, oxides or hydroxides of copper to be enhanced by the addition of terpenic derivatives because of the difference in physicochemical nature between the inorganic salts, oxides or hydroxides of copper, on the one hand, and the sulfur metal species, on the other hand, in particular because of the fact that sulfur is essentially lipophilic, while the inorganic salts, oxides or hydroxides of copper are essentially hydrophilic.

The subject of the invention is a fungicidal, bactericidal or bacteriostatic plant-protection composition comprising at least one inorganic salt, one oxide or one hydroxide of copper in suspension in an aqueous emulsion of at least one terpenic derivative.

The aqueous emulsions also cover the microemulsions.

The inorganic salt, oxide or hydroxide of copper consists of one or of a mixture of those mentioned above, copper hydroxide ($Cu(OH)_2$) being preferred.

The terpenic derivatives for the purposes of the present invention are organic molecules containing ten carbon atoms in their structure.

They are therefore essentially monoterpenes.

The terpenic derivatives may be acyclic, monocyclic or bicyclic.

The following examples may be mentioned in particular:

1) the terpenic hydrocarbons:

a) acyclic terpenic hydrocarbons: myrcene, alloocimene, and the like;

b) monocyclic terpenic hydrocarbons: dipentene, terpinolene, p-cymene, limonene, and the like;

c) bicyclic terpenic hydrocarbons: α-pinene, β-pinene or δ-3-carene, and the like;

2) the following compounds:

a- the oxidized derivatives: cineols;

b- the terpenic alcohols: borneol, fenchol, menthanol, terpineols, geraniol, 1-terpinen-4-ol, and the like;

c- the aldehydes and ketones: camphor, fenchone;

3) the mixtures of the products cited above;

4) the essential oils containing the above mixtures in various proportions, for example *Malalenca alternifolia* essential oil (or tea-tree oil);

5) the pine oils of natural or synthetic origin which are defined as being mixtures of terpenic hydrocarbons and alcohols.

Pine oil containing 90% of terpenic alcohols is most particularly preferred.

The suspension according to the invention advantageously also contains at least one surfactant for its emulsifying, wetting, crystal growth inhibiting properties, and the like.

It is possible to use an anionic, cationic, amphoteric, zwitterionic and/or nonionic surfactant.

The anionic and nonionic surfactants, alone or in the form of a mixture, are preferred.

The following compounds are particularly well suited to the aim of the invention:

- ethoxylated fatty acids,
- ethoxylated fatty alcohols,

- calcium alkylbenzenesulfonate,
- alkylnaphthalenesulfonates,
- ethoxylated alkylphenols,
- EO/PO block copolymers,
- PO/EO block copolymers,
- diisopropylnaphthalenesulfonates,
- dimethylnaphthalenesulfonates,
- di-n-butylnaphthalenesulfonates,
- ethoxylated dodecylphenols,
- sodium dodecylbenzenesulfonate,
- phosphoric esters of alkyl polyethers (acid forms and/or salts),
- phosphoric esters of ethoxylated arylphenols (acid forms and/or salts),
- phosphoric esters of ethoxylated polyarylphenols (acid forms and/or salts),
- ethoxylated castor oil,
- isopropylnaphthalenesulfonates,
- lignosulfonates,
- methyldinapthalenesulfonates,
- methylnaphthalenesulfonates,
- n-butylnapthalenesulfonates,
- ethoxylated octylphenols,
- phenyl sulfonates,
- polyalkylnaphtylmethanesulfonates,
- polyacrylates,
- ethoxylated polyarylphenols,
- polycarboxylates,
- polyvinylpyrrolidone and derivatives thereof,
- salts of sulfonated cresol-formalin condensates,
- salts of condensates of naphthalenesulfonic acid,
- salts of acrylic acid-acrylic ester copolymers,
- salts of maleic acid-olefin copolymers,
- salts of maleic anhydride-isobutylene copolymers,

- ethoxylated alkylphenol sulfates,
- ethoxylated polyarylphenol sulfates,
- sulfosuccinates,
- taurates,
- ethoxylated tristyrylphenols...

The suspension concentrates of the present invention advantageously comprise from 200 to 600 g/l, preferably 300 to 500 g/l of copper, of the inorganic salt, oxide or hydroxide of copper expressed relative to the copper element. The contents of terpenes in the formulations are between 50 and 400 g/l, preferably 80 to 200 g/l.

The contents of surfactant(s) in the formulations are between 20 and 100 g/l, preferably 30 to 60 g/l.

The liquid compositions of the invention, also called suspension concentrates or "flowable concentrates" may be prepared by micronizing the active substance, optionally mixed with a portion or all of the other ingredients, by passing through a specific mill (for example a ball mill of the ®DYNO-MILL type) until a stable homogeneous suspension is obtained.

Mechanical micronization may be avoided and a simple mixing may be sufficient if an active substance which is already micronized either mechanically or by the method of synthesis, is used. In either case, the micronization is performed until a diameter of the particles of inorganic salts, oxides or hydroxides of copper not greater than 6 μm is obtained.

An example of copper hydroxide which may be suitable for the preparation of a composition by simple mixing is the technical copper hydroxide manufactured by NORDEUTSCHE AFFINERIE, marketed by URANIA AGROCHEM GmbH.

It is also possible to use a copper hydroxide prepared in accordance with the methods described in US 3,194,749 and US 4,944,935.

The compositions of the invention have a markedly improved fungicidal, bactericidal or bacteriostatic activity compared with the compositions of the state of the art not containing a terpenic derivative.

This gain in efficacy makes it possible to reduce the quantities of copper applied to the plants during treatments.

This dose reduction is very advantageous because it makes it possible to reduce the sometimes depressive action which copper exerts on plants and its phytotoxicity toward some plants.

The subject of the invention is also the use of a terpenic derivative for enhancing the efficacy of an inorganic salt, an oxide or a hydroxide of copper in a plant-protection, in particular fungicidal, bactericidal or bacteriostatic, composition.

The subject of the invention is, furthermore, a method of treating plants with a product based on an inorganic salt, oxide or hydroxide of copper, characterized in that an effective quantity of plant-protection mixture prepared by mixing, in aqueous form, a composition of an inorganic salt, oxide or hydroxide of copper in suspension in an aqueous emulsion containing at least one terpenic derivative, is sprayed on the plant to be treated.

Examples of compositions based on an inorganic salt, oxide or hydroxide of copper and a terpene according to the invention as well as the results obtained with these compositions on vine downy mildew (*Plasmopara viticola*) will be given below.

Examples 1 to 3 of compositions according to the invention

	Formula A		Formula B		Formula C	
	Content of copper: from 300 to 310 g/l					
Copper hydroxide	36.76%	501 g/l	36.76%	500 g/l	36.76%	500 g/l
Pine oil (containing 90% of terpenic alcohols)	6.60%	90 g/l	9.78%	133 g/l	12.94%	176 g/l
Urea	4.00%	54.5 g/l	4.00%	54.4 g/l	4.00%	54.4 g/l
TENSIOFIX® BCZ (sulfated alcohol)	1.00%	13.6 g/l	1.00%	13.6 g/l	1.00%	13.6 g/l
TENSIOFIX® LX (lignosulfonate)	1.00%	13.6 g/l	1.00%	13.6 g/l	1.00%	13.6 g/l
TENSIOFIX® D40 (cationic/nonionic surfactant)	1.00%	13.6 g/l	1.00%	13.6 g/l	1.00%	13.6 g/l
Silcone-containing antifoam	0.05%	0.7 g/l	0.05%	0.7 g/l	0.05%	0.7 g/l
BARAGEL® 24	1.50%	20.5 g/l	1.00%	13.6 g/l	0.50%	6.8 g/l
Water	48.09%	656.1 g/l	45.41%	617.5 g/l	42.75%	581.4 g/l

Active substance: Technical copper hydroxide (content of copper: 62.05%)

Composition prepared by mixing the various ingredients and then micronizing by passing through a mill of the ®DYNO-MILL type.

TENSIOFIX®: OMNICHEM trademark

BARAGEL®: NL-CHEMICAL trademark.

Example 4: Example of composition according to the invention

	Formula D	
	Content of copper: 396.1 g/l	
Copper hydroxide	43.55%	659 g/l
Pine oil (containing 90% of terpenic alcohols)	8.62%	130.5 g/l
Polyarylphenol phosphate which is ethoxylated and neutralized with triethanolamine	1.67%	25.3 g/l
Aqueous solution containing 35% of a sodium salt of a sulfonated cresol-formalin condensate	4.91%	74.3 g/l
Monoethylene glycol	5.84%	88.4 g/l
Heteropolysaccharide of the xanthan gum type	0.11%	1.7 g/l
Silicone-containing antifoam	qs	qs
Water	qs 100	qs 100

Active substance: Technical copper hydroxide (content of copper = 62.4%) marketed by URANIA AGROCHEM GmbH

- Particle size
  - < 13 µm: 100%
  - < 6.6 µm: 92.4%
  - < 4.7 µm: 81.5%
  - < 3.3 µm: 64.8%
  - < 2.4 µm: 47.6%

Composition prepared by simple mixing of the various ingredients.

Example 5: Example of composition according to the invention

	Formula E	
	Content of copper: 407 g/l	
Copper hydroxide	45.00%	691.2 g/l
Pine oil (containing 90% of terpenic alcohols)	7.80%	119.8 g/l
Polyarylphenol phosphate which is ethoxylated and neutralized with triethanolamine	2.20%	33.8 g/l
Aqueous solution containing 35% of a sodium salt of a sulfonated cresol-formalin condensate	5.00%	76.8 g/l
Glycerol	1.40%	21.5 g/l
Urea	6.00%	92.2 g/l
Silicone-containing antifoam	qs	qs
Heteropolysaccharide of the xanthan gum type	0.125%	1.9 g/l
Water	qs 100	qs 100

Active substance: Technical copper hydroxide (content of copper = 62.88%)

Composition prepared by mixing the various ingredients and then micronizing by passing through a ball mill of the ®DYNO-MILL type.

Example 6: Results of experimentation on vine downy mildew (*Plasmopara viticola*)

-1st trial: Scores on leaves

	Dose/ha of Product	Doses/ha		% of damage on leaves	
		Copper	Pine oil	1st score	2nd score
NTC	/	/	/	68.75%	97.50%
Formula B	5 l	1500 g	665 g	43.75%	83.75%
Formula C	5 l	1500 g	880 g	40.63%	84.38%
Formula A	7.5 l	2250 g	675 g	43.13%	85.63%
Formula B	7.5 l	2250 g	998 g	29.38%	70.63%
Formula C	7.5 l	2250 g	1320 g	26.25%	68.13%
SC formulation (state of the art)	8.8 l	3000 g	/	38.13%	82.50%
WP formulation (state of the art)	6 kg	3000 g	/	42.50%	78.13%

Study on young plants

Grape vine, Cabernet-Sauvignon cultiver

Trials under misting with artificial contaminations

NTC: Non treated control SC: Suspension concentrate

WP: Wettable powder

-<u>2nd trial</u>: Scores on bunches of grapes

	Dose/ha of Product	Doses/ha		1st score		2nd score	
		Copper	Pine oil	Intensity	Frequency	Intensity	Frequency
NTC	/	/	/	72.85%	14.29%	98.20%	58.56%
Formula D	5 l	2050 g	650 g	6.41%	0.33%	27.50%	2.29%
SC formulation (state of the art)	6.7 l	2030 g	/	9.09%	0.75%	36.03%	2.82%

Study on fruit-bearing plants

Grape vine, Cabernet-Sauvignon cultiver

Trials under misting with artificial contaminations

NTC: Non treated control SC: Suspension concentrate

-**3rd trial: Scores on leaves**

	Dose/ha of Product	Doses/ha		% of damage on leaves	% of defoliating
		Copper	Pine oil		
Formula D	5 l	2050 g	650 g	22.50%	48.75%
SC formulation (state of the art)	6.7 l	2030 g	/	36.25%	60.00%

Study on fruit-bearing plants
Grape vine, Cabernet-Sauvignon cultiver
Trials under misting with artificial contaminations
SC: Suspension concentrate

-**4th trial: Scores on leaves**

	Dose/ha of Product	Doses/ha		1st score		2nd score		3rd score	
		Copper	Pine oil	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency
NTC	/	/	/	15.0%	64.5%	62.83%	99.0%	58.65%	84.0%
Formula E	4 l	1630 g	480 g	1.8%	6.8%	1.63%	16.0%	1.47%	14.3%
Formula E	5 l	2040 g	600 g	1.5%	6.8%	0.90%	9.0%	1.33%	15.0%
Formula E	6.25 l	2540 g	750 g	2.2%	8.5%	1.22%	11.5%	1.16%	11.0%
SC formulation (state of the art)	7 l	2520 g	/	2.0%	8.8%	2.20%	19.0%	1.91%	15.3%

Study on fruit-bearing plants
Grape vine, Grenache
Trials under misting with artificial contaminations
NTC: Non treated control SC: Suspension concentrate

-<u>5th trial</u>: Scores on bunches of grapes

	Dose/ha of Product	Doses/ha		1st score		2nd score	
		Copper	Pine oil	Intensity	Frequency	Intensity	Frequency
NTC	/	/	/	9.90%	57.5%	67.70%	99.8%
Formula E	4 l	1630 g	480 g	0.20%	2.3%	7.05%	42.8%
Formula E	5 l	2040 g	600 g	0.15%	2.6%	7.30%	36.3%
Formula E	6.25 l	2540 g	750 g	0.01%	0.5%	1.70%	14.8%
SC formulation (state of the art)	7 l	2520 g	/	9.09%	1.5%	4.10%	29.5%

Study on fruit-bearing plants

Grape vine, Grenache

Trials under misting with artificial contaminations

NTC: Non treated control SC: Suspension concentrate

-6th trial: Scores on leaves

	Dose/ha of Product	Doses/ha		1st score		2nd score		3rd score	
		Copper	Pine oil	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency
NTC	/	/	/	24.3%	84.5%	27.83%	97.8%	27.34%	91.8%
Formula E	4 l	1630 g	480 g	0.6%	3.5%	0.90%	4.5%	0.35%	2.3%
Formula E	5 l	2040 g	600 g	0.2%	2.3%	0.23%	2.3%	0.17%	1.3%
SC formulation (state of the art)	7 l	2520 g	/	0.2%	2.0%	0.45%	2.0%%	0.18%	2.0%

Study on fruit-bearing plants
Grape vine, Grenache
Trials under misting with artificial contaminations
NTC: Non treated control SC: Suspension concentrate

-<u>7th trial</u>: Scores on bunches of grapes

	Dose/ha of Product	Doses/ha		Intensity	Frequency
		Copper	Pine oil		
NTC	/	/	/	6.5%	39.8%
Formula E	4 l	1630 g	480 g	0.1%	0.8%
Formula E	5 l	2040 g	600 g	0.1%	0.4%
Formula E	6.25 l	2540 g	750 g	0.0%	0.4%
SC formulation (state of the art)	7 l	2520 g	/	0.1%	0.9%

Study on fruit-bearing plants

Grape vine, Grenache

Trials under misting with artificial contaminations

NTC: Non treated control SC: Suspension concentrate